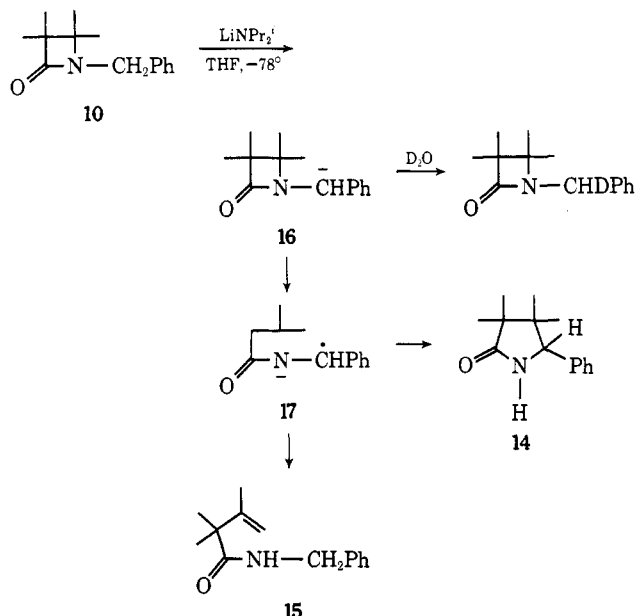


Reaction of **10** with lithium diisopropylamide at -78° for 1 min followed by treatment with D_2O yielded recovered **10** bearing one deuterium in the benzylic position. When the reaction mixture was allowed to warm to room temperature, or when the reaction was carried out at room temperature, the pyrrolidone **14**¹² and the acyclic amide **15**¹³ were obtained in 90% yield (approximate ratio 1:1). A rationalization of these results involving the intermediacy of a benzylic carbanion and radical-radical anion **17** is shown below.¹⁴



Acknowledgment. The financial support of Bristol Laboratories, Syracuse, N. Y., and the National Research Council of Canada is gratefully acknowledged.

(12) Compound **14** showed the following properties: colorless needles; mp $119-120^\circ$; ir (CHCl₃) 3435 and 1700 cm^{-1} . The nmr spectrum showed singlets at δ 0.42 (3 H), 0.93 (6 H), 1.08 (3 H) and 4.48 (1 H), and 6.1 (NH), and a multiplet from δ 7.1 to 7.4 (5 H).

(13) Compound **15**, colorless oil, had strong ir bands (CHCl₃) at 3435, 1655, 1638, and 903 cm^{-1} ; nmr peaks were at δ 1.33 (s, 6 H), 1.73 (br s, 3 H), 4.39 (d, $J = 5.0$ Hz, 1 H), 4.9–5.0 (m, 2 H), 5.0 (NH), and 7.23 (s, 5 H).

(14) The product **15** could conceivably have arisen from the anion **16** via an intramolecular E1cb elimination.

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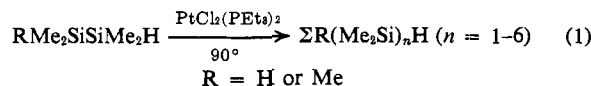
Received August 14, 1972

Dichlorobis(triethylphosphine)nickel(II) as a Catalyst for Reactions of *sym*-Tetramethyldisilane with Unsaturated Hydrocarbons. Novel Synthetic Routes to 1-Silacyclopentadienes and 1,4-Bis(dimethylsilyl)-2-butenes

Sir:

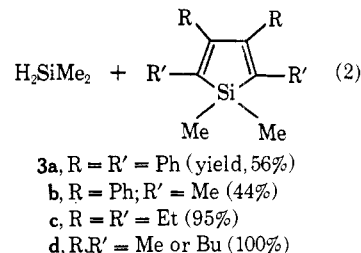
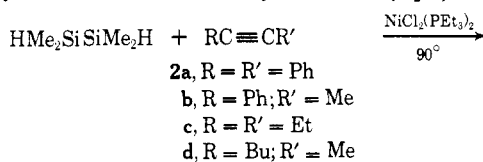
In recent years the hydrosilylation of olefins has been effectively achieved through a process employing a group VIII metal complex as an active homogeneous catalyst. It has been suggested¹ that one of the essential steps in the hydrosilylation process is the oxidative addition of the hydrosilane to the metal complex which originally contains the metal in a low oxidation state. Interestingly, however, none of the reactions of

hydrosilanes, such as pentamethyldisilane and *sym*-tetramethyldisilane, with metal complexes occur without cleavage of the silicon-silicon bond.^{2,3} For example, methyldisilicon hydrides disproportionate in the presence of a platinum(II)⁴ as indicated by eq 1.



We have suggested there that the reaction most likely involves an α elimination of the methyldisilicon hydride with loss of "dimethylsilylene,"⁵ which inserts into the silicon-hydrogen bond present in the original reagent. Evidence for this suggestion has been provided by the fact that the silylene species formed on the platinum catalyst is trapped by diphenylacetylene to give 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (**1**)⁷ in low yield (ca. 5%).^{4b}

We now wish to report that dichlorobis(triethylphosphine)nickel(II) catalyzes the reaction of *sym*-tetramethyldisilane with a variety of disubstituted acetylenes to give 1-silacyclopentadiene derivatives in good yield based on the acetylene used (eq 2).



Thus, a mixture of *sym*-tetramethyldisilane (2 mmol), diphenylacetylene (2 mmol), and 5 mg of $NiCl_2(PEt_3)_2$ dissolved in 1.5 ml of dry cyclohexane was heated for 18 hr at 90° in a degassed sealed glass tube. On cooling the reaction mixture, green-yellow crystals precipitated. Filtration and washing of the precipitate with a little cyclohexane gave 234 mg (56% yield) of practically pure 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**3a**), mp $178-179^\circ$ (lit.⁸ mp $181-182^\circ$).

Similarly, use of 1-phenyl-1-propyne, 3-hexyne, or 2-heptyne gave 1-silacyclopentadiene derivatives (**3b-3d**) that are all new and otherwise hardly accessible. Structures have been assigned on the basis of uv and nmr spectra.⁹ With 2-heptyne a mixture of three pos-

(2) D. Kummer and J. Furrer, *Z. Naturforsch. B*, **26**, 162 (1971).

(3) A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971).

(4) (a) K. Yamamoto, H. Okinoshima, and M. Kumada, *J. Organometal. Chem.*, **23**, C7 (1970); (b) *ibid.*, **27**, C31 (1971).

(5) The silylene may be by no means a free divalent silicon species,⁶ but complexed with platinum.

(6) For pertinent reviews see, e.g., W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(7) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968), and references cited therein.

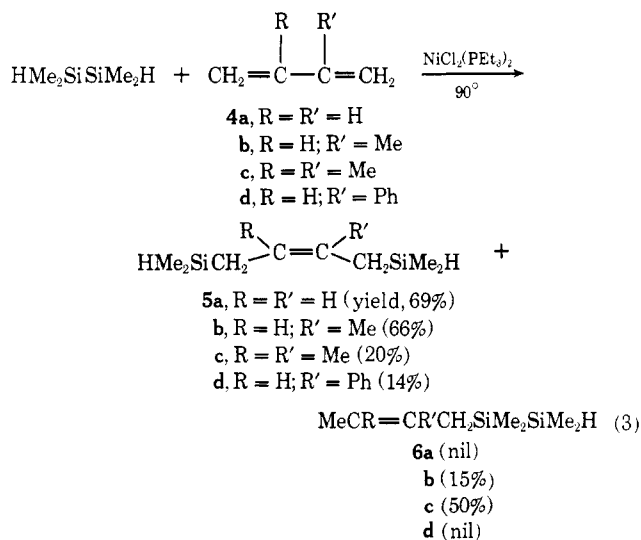
(8) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).

(9) For example, **3b**: uv max (cyclohexane) 236 nm (ϵ 16,000) and 306 (ϵ 1900); nmr (CCl₄) δ 6.66–7.10 (diffused, 10, Ph), 1.80 (s, 6, Me), and 0.27 ppm (s, 6, SiMe). **3c**: uv max (cyclohexane) 300.5 nm (ϵ 2500); nmr (CCl₄) δ 2.26 (q, 4, $J = 7.6$ Hz, CH_2Me in α), 2.21 (q, 4, $J = 7.6$ Hz, CH_2Me in β), 1.03 (t, 6, $J = 7.6$ Hz, Me in α), 0.98 (t, 6, $J = 7.6$ Hz, Me in β), and 0.17 ppm (s, 6, SiMe).

(1) A. J. Chalk, *Trans. N. Y. Acad. Sci.*, **32**, 481 (1970).

sible isomers, **3d** ($R = \text{Me}$; $R' = \text{Bu}$), **3d** ($R = \text{Bu}$; $R' = \text{Me}$), and **3d** ($R, R' = \text{alternate Me and Bu}$), was obtained in a ratio of 32:12:56. It should be noted that without added acetylene, the disproportionation of *sym*-tetramethyldisilane proceeded with accumulation of the trisilane (cf. eq 1). Furthermore, when dimethyl acetylenedicarboxylate was employed as the acetylene compound, we found that none of the product arising from incorporation of the dimethylsilylene moiety into the acetylene was formed. Further, the redistribution of the disilane did not occur. Methyl melitate was a sole product. The data suggest that dialkyl- and diarylacetylenes react with "dimethylsilylene" under mild conditions in the presence of a nickel catalyst. In contrast, dimethyl acetylenedicarboxylate does not react in a similar manner. We believe that the latter fact results from such strong coordination of the dimethyl acetylenedicarboxylate by the nickel complex catalyst that oxidative addition of the disilane is blocked. Under these conditions "dimethylsilylene" would not be formed.

The reaction of *sym*-tetramethyldisilane with a variety of butadienes has also been studied in the presence of the same nickel catalyst. The reaction with butadiene has been found to give a major product which is doubly silylated at the 1,4 positions of the diene. In some cases, considerable amounts of the hydrosilylation product are also formed. The 1,4-double silylation process tends to be counteracted by the hydrosilylation process (eq 3).

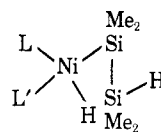


The observed reactions involving *sym*-tetramethyldisilane, an olefinic or acetylenic compound, and a phosphine-nickel(II) complex fall into four types: (i) disproportionation proceeding in the presence or absence of an olefinic compound to form several homologous members of polysilanes of the formula $\text{H}(\text{Me}_2\text{Si})_n\text{H}$; (ii) simple addition of the silicon-hydrogen bond across an olefinic bond (hydrosilylation);¹⁰ (iii) generation of "dimethylsilylene" species, which are effectively trapped by an added acetylenic compound; and (iv) cleavage of the silicon-silicon bond followed by 1,4 addition of

(10) There has been preliminary evidence that the metal complex catalysts cause the hydrogen-silicon bond to scramble as well as labilize the silicon-silicon bond of *sym*-tetramethyldisilane. The observed hydrosilylation of butadiene without cleavage of the silicon-silicon bond should be noted in this regard.

the resultant silyl groups (double silylation). These four processes may well be interrelated to each other from the mechanistic point of view.

The novel feature about these reactions can be visualized as proceeding *via* the following steps. First, there occurs oxidative addition of *sym*-tetramethyldisilane to the nickel catalyst. (It is assumed that the metal atom is in a low oxidation state as a result of initial reduction by the silicon hydride.) The following highly active intermediate **7** is then postulated



7, $L, L' =$ phosphine or unsaturated hydrocarbon ligands

Subsequently, either elimination of dimethylsilane to leave the "dimethylsilylene" on nickel or cleavage of the silicon-silicon bond to form a bis(dimethylsilyl)-nickel complex is assumed. An alternative pathway for the formation of 1,4-bis(dimethylsilyl)-2-butenes is also conceivable. This involves initial addition of "dimethylsilylene" to butadiene to give 1-dimethylsilylbutadiene¹¹ which then undergoes hydrosilylation with dimethylsilane produced as a result of the α elimination of *sym*-tetramethyldisilane.

(11) Skell and Goldstein¹² have reported that dimethylsilylene adds to ethylene to give dimethylvinylsilane by rearrangement.

(12) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

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Fragmentation of Phosphoranes

Sir:

Several methods are now available for the synthesis of pentavalent phosphorus compounds¹⁻⁶ and of these the routes *via* condensation of trivalent phosphorus compounds with (a) α -dicarbonyl compounds and (b) diethyl peroxide² are the most well established. For the second reaction a considerable body of evidence is accumulating to indicate that the reaction is a concerted biphilic addition of the peroxide to trivalent phosphorus *via* a transition state represented by **1**.^{7,8} The geometry of the transition state is, however, unknown.

The reaction of 3-methyl-1-phenyl-3-phospholene (**2**) with diethyl peroxide takes an unusual course in that the phosphorane (**3**) formed initially fragments

(1) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(2) (a) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, **91**, 5243 (1969).

(3) B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *ibid.*, **93**, 4004 (1971).

(4) M. Sanchez, L. Beslier, J. Roussel, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3053 (1969).

(5) J. Wilff and R. Huisgen, *Chem. Ber.*, **102**, 1841 (1969).

(6) W. G. Bentrude, W. D. Johnson, and W. A. Khan, *J. Amer. Chem. Soc.*, **94**, 3058 (1972).

(7) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *ibid.*, **94**, 245 (1972).

(8) D. B. Denney, private communication.